10528p

(19) Europäisches Pat ntamt
European Pat nt Offic
Office européen des br v ts

(11) Publication number : **0 557 250 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : 93830011.8

(22) Date of filing : 15.01.93

(51) Int. Cl.[5] : **H01M 6/18, H01B 1/12, G02F 1/15**

(30) Priority : 17.01.92 IT RM920036

(43) Date of publication of application : 25.08.93 Bulletin 93/34

(84) Designated Contracting States : AT BE CH DE DK ES FR GB GR IE LI LU MC NL PT SE

(71) Applicant : ENEA ENTE PER LE NUOVE TECNOLOGIE, L'ENERGIA E L'AMBIENTE
Viale Regina Margherita, 125
I-00198 Roma (IT)

(72) Inventor : Scrosati, Bruno
Via Abbadia S. Salvatore 16
I - 00189 Rome (IT)
Inventor : Croce, Fausto
Via L. Pirandello 72
I - 00137 Rome (IT)
Inventor : Capuano, Federico
Via Atina, 16
I - 00189 Rome (IT)

(74) Representative : Sarpi, Maurizio
Studio FERRARIO Via Collina, 36
I-00187 Roma (IT)

(54) Composite polymeric electrolyte, in particular for use in light-weight electrochemical accumulators.

(57) Composite, ternary, polymeric system formed by intimately mixing a polymeric compund, a metal salt, and a ceramic additive acting both as agent promoting the transport features (conductivity and ion mobility) and as stabilizer of the chemical characteristics (compatibility with the electrode materials) of the polymeric electrolyte.

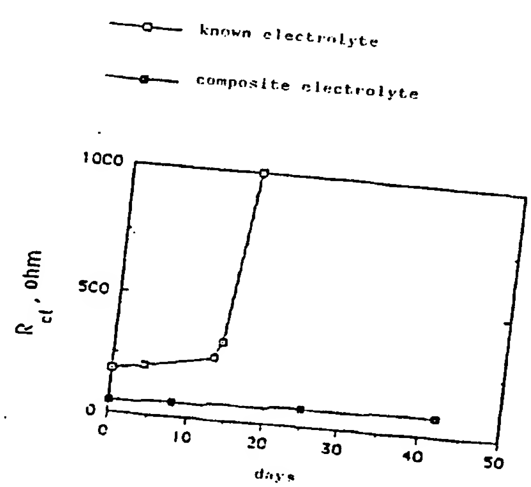

FIG. 3

EP 0 557 250 A1

The present invention relates to a composite polymeric electrolyte, in particular for use in light-weight electrochemical accumulators.

At the present state of art the use of complex compounds formed of polymeric components, e.g. lithium salts, such as electrolytic membranes for manufacturing electrochemical thin-layer devices (for example accumulators or optical detectors) is known. The use of such complex compounds is, however, limited in part by the operating temperature generally higher than 80°C and by the chemical action to the used electrode materials, in particular to lithium. The high temperature is bound to the transport mechanism which requires a polymeric structure having an amorphous state to a certain extent which is reached only above 80°C in the known systems.
The reactivity to the electrode materials is bound to the presence of impurities (for example, water and/or solvents having low boiling point) which can hardly be eliminated by means of simple purification systems. It is then very important to find alternate materials leading to an increase of the electrical conductivity and thermal stability of the polymeric electrolytes.

According to the invention it is provided a modification of the known systems by the addition of ceramic dust (preferably crystal zeolites, usually referred to as "molecular sieves" whose general formula is $Me_{x/n}(A10_2)_x$ $(Si0_2)_y.xH_20$, where Me = K, Na, Ca,..., and x, y and n are integers). If such sieves have suitable dimensions and concentrations (for example, type A4), they promote the formation of amorphous phases (thus increasing the conductivity at low temperatures) and the compounding of impurities which ar then separated from the electrolyte, thus increasing the stability to the electrode materials.

The composite, ternary polymeric electrolyte according to the invention is prepared by dispersing into a solution of a suitable solvent (for example acetonitrile) the three components, i.e. the polymeric component (e.g. ethylene poly(oxide)), the metal salt component (e.g. lithium perchlorate) and the ceramic additive (e.g. molecular sieves) in suitable proportions, for example according to the weight ratio of 10:20:70 referred to ceramic additive/polymer/salt. The dispersion is homogenized, concentrated and poured onto a substrate of inert material, for example plastic material. The solvent is then further evaporated until a self-sustaining membrane is formed.
The addition of a ceramic additive causes three essential improvements over the known compositions, i.e. the electrolytes formed only by the combination of the polymeric component and the metal salt. Such improvements forming the characterizing part of th present invention are shown in the accompanying drawings and disclosed in the following d scription.

In the drawings:

Fig. 1 is a diagram of the mechanical stability of the composite electrolyte according to th invention and that of a known electrolyte;

Fig. 2 is a diagram of the conductivity of the composite electrolyte according to the invention and that of a known electrolyte;

Fig. 3 is a diagram of the impedances of lithium cells based upon the composite electrolyte according to the invention and the known electrolyte.

The improvements achieved by the composite electrolyte of the present invention are as follows.

A) Increase in the mechanical characteristics. The dispersion of the ceramic additive leads to the development of a solid matrix which enhances as a whole the mechanical stability of the electrolyte. This effect is experimentally proved by the diagram of Fig. 1 showing a comparison between the stability in the time of the resistance of the composite electrolyte according to the invention and that of a known electrolyte. The measurement has been carried out by means of cells under pressure and then the reduction in the resistance indicates a reduction in the distance between the electrodes, which is to be referred to the fluidity of the electrolytic material.
From, Fig. 1 of the annexed drawing it is evident that the mechanical stability of the composite electrolyte is greater than that of the known electrolytic. Such feature makes the composite electrolyte capable of being easily shaped and then it is preferably used for devices of practical application.

B) Increase in the conductivity. The presence of the additive under the form of particles of small diameter dispersed in the system inhibits the crystallization of the chains of the polymeric component and promotes the formation of an amorphous structure, which is essential for assuring a fast ion mobility.
Such improvement, which is of basic importance for the technological applications as it allows low temperatures to be applied, is proved in Fig. 2 in which the conductivity of the composite electrolyte according to the invention and that of the known electrolyte are compared.

C) Increase in the chemical stability. The ceramic additive entraps the traces of water impurities, thus taking them away from the electrolyte, by virtue of the well-known hydrophile characteristics. As the impurities are responsible for the etching of the electrode materials and in particular the metal lithium, their removal gives the composite electrolyte a greater inertia over the conventional electrolyte. This is proved in Fig. 3 which compares the impedances of symmetric lithium cells based upon both above-mentioned electrolytes. It is seen in the figure that the resistance of the interfac electrode/electrolyte d signated by Rct increases in the time in case of cells with conventional electrolyte but remains substantially constant in cas of cells with composite electrolyte.
The results prov that in th first cas ther is a progressive etching to lithium causing a growth of a pas-

sivating layer on the surface thereof, while in the second case th condition of th interphas remains nearly constant. As the electrodic passivation leads to a d cay of the cell performance, its elimination is a substantial improvement and assures the development of devices exhibiting a long useful life.

The present invention is described with reference to a preferred embodiment thereof, however, it should be understood that modifications can be made by those skilled in the art without departing from the scope of the present invention.

Claims

1. A composite ternary, polymeric electrolyte, wherein it is formed by combining a polymeric component, a metal salt, and a ceramic additive.

2. The electrolyte of claim 1, characterized in that the polymeric component is ethylene poly(oxide).

3. The electrolyte of claims 1, characterized in that the metal salt is lithium perchlorate.

4. The electrolyte of claim 1, characterized in that the ceramic additive is a molecular sieve.

5. The electrolyte of claim 1, characterized in that the weight ratio among ceramic additive, polymer and metal salt is preferably 10:20:70.

6. The electrolyte of claim 1, characterized in that the polymeric component is formed of polymer chains containing oxygen and sulphur atoms.

7. The electrolyte of claim 1, characterized in that the metal salt is selected from the class of mono- and/or multivalent metal salts.

8. The electrolyte of claim 1, characterized in that the additive is formed of a substituted zeolite or other suitable ceramic compound.

9. The electrolyte of claims 1, 4 and 8, characterized in that the additive is in the form of particles of small diameter dispersed in the system so as to inhibite the crystallization of the chains of the polymeric component and to permit the use thereof at low temepratures.

10. A composite, ternary, polymeric electrolyte according to the preceding claims, wherein it is prepared in the form of an electrolytic membrane by dispersing the three components into a solution of a suitable solvent, homogenizing and concentrating such solution, pouring the dispersion onto a substrate of inert material and further evaporating the solvent until a self-sustaining membrane is formed.

11. Use of the composite polymeric electrolyte of th preceding claims in electrochemical high-en rgy accumulators.

12. Use of the composite polymeric electrolyte of claims 1 to 10 in optical thin-layer detectors.

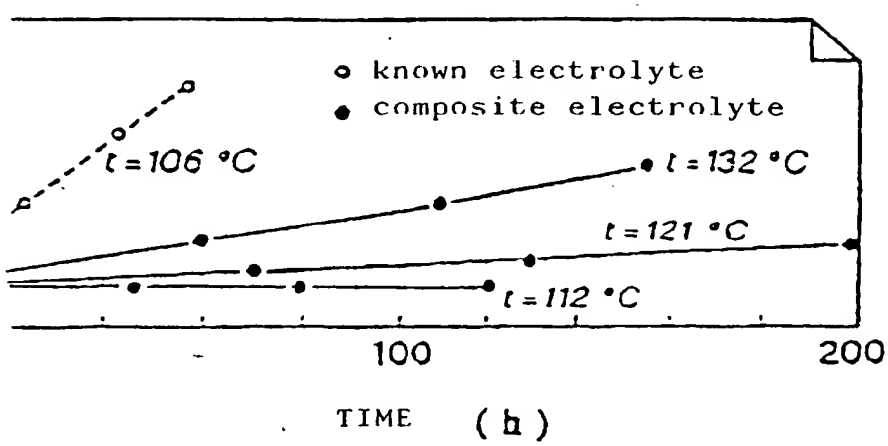
known electrolyte
composite electrolyte
t = 106 °C
t = 132 °C
t = 121 °C
t = 112 °C
100
200
TIME (h)

FIG. 1

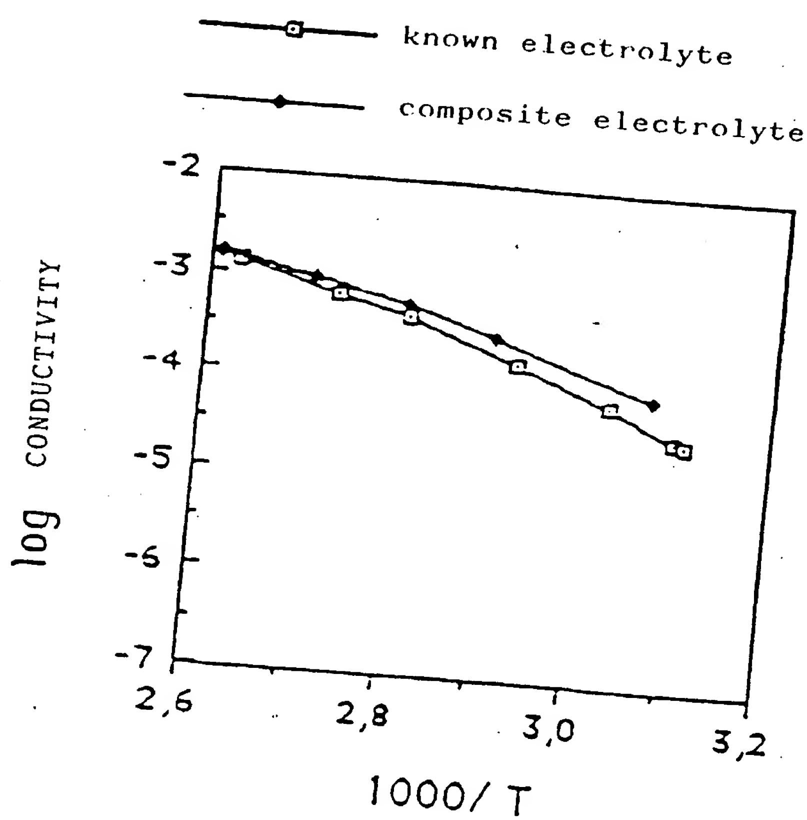
known electrolyte
composite electrolyte
log CONDUCTIVITY
-2
-3
-4
-5
-6
-7
2,6
2,8
3,0
3,2
1000/ T

FIG. 2

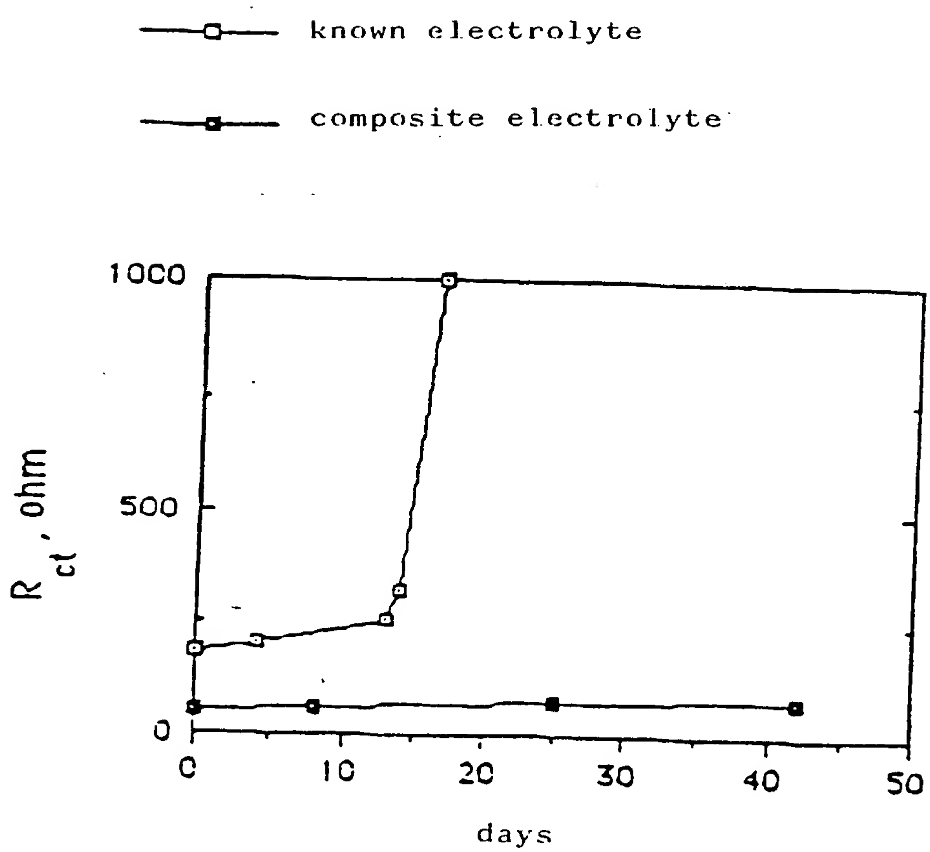
known electrolyte
composite electrolyte
1000
500
0
R_{ct}, ohm
0
10
20
30
40
50
days

FIG. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 83 0011
Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	JOURNAL OF POWER SOURCES. vol. 32, no. 4, 1990, LAUSANNE CH pages 381 - 388 F. CROCE ET AL 'The Lithium Polymer Electrolyte Battery IV. Use of Composite Electrolytes' * the whole document *	1-3,7, 9-11	H01M6/18 H01B1/12 G02F1/15
X	SOLID STATE IONICS vol. 40/41, no. 1, August 1990, AMSTERDAM NL pages 375 - 379 F. CROCE ET AL 'Properties and Applications of Lithium Ion-Conducting Polymers' * the whole document *	1-3,7, 9-12	
X	SOLID STATE IONICS vol. 7, no. 1, August 1982, AMSTERDAM NL pages 75 - 79 J. E. WESTON ET AL 'Effects of Inert Fillers on the Mechanical and Electrochemical Properties of Lithium Salt-Poly(Ethylene Oxide) Polymer Electrolytes' * the whole document *	1-3,7,9, 10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	SOLID STATE IONICS vol. 28-30, no. II, September 1988, AMSTERDAM NL pages 979 - 982 J. PLOCHARSKI ET AL 'PEO Based Composite Solid Electrolyte Containing Nasicon' * the whole document *	1,2,7,9, 10	H01M
	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 APRIL 1993	M. P. ANDREWS

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 83 0011
Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	SOLID STATE IONICS vol. 36, no. 3/4, November 1989, AMSTERDAM NL pages 255 - 257 W. WIECZOREK ET AL 'Modifications of Crystalline Structure of PEO Polymer Electrolytes with Ceramic Additives' * the whole document *	1,2,7,9, 10	
A	EP-A-0 379 372 (MBH JOINT VENTURE) * page 6, line 23; claims 1,7,8 *	1,2,11	
A	GB-A-2 030 351 (THE SOUTH AFRICAN INVENTIONS DEVELOPMENT CORPORATION) * claims 9,14,17 *	1,6,8,11	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 117 (E-498)11 April 1987 & JP-A-61 264 679 (MATSUSHITA) * abstract *	1,4,11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 173 (P-87)5 November 1981 & JP-A-56 102 830 (NEC) * abstract *	1,4,12	
A	CHEMICAL ABSTRACTS, vol. 113, no. 2, 1989, Columbus, Ohio, US; abstract no. 7841k, FENGLIANG LIN ET AL 'Ion Conductive Silicate-Containing Plastic Membranes' * abstract * & CN-A-1 034 212 (CHINESE SCIENTIFIC AND TECHNOLOGICAL UNIVERSITY)	1,4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 APRIL 1993	M. P. ANDREWS

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document